Crystal Structure Analysis of C60 Low Temperature Phase by Electron Crystallography with Cryo-TEM (STATES AND STRUCTURES-Crystal Information Analysis)

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The crystal structure of C_{60} at liquid helium temperature was examined by electron diffraction method using an imaging plate and cryo-TEM. The R factor could be reduced to a certain amount by assuming a multi-component crystal. Disorder in the crystal might be an important factor as well as dynamical scattering effect to be considered in electron crystallography for analyzing structures of thin crystals.

Keywords: Electron crystallography / C_{60} / Cryo-TEM / Imaging plate

A transmission electron microscope (TEM) is a useful tool for studying crystal structures of ultra-thin organic specimens. Recently, Dorset and coworkers [1] demonstrated the possibility of crystal structure analysis by the electron diffraction technique. However, the kinematical treatment gives only 0.2-0.3 as the R factor, which is worse compared with the results of X-ray or neutron scattering methods. The reason is considered to be the existence of dynamical scattering and the lack of quantitative response of the conventional recording medium. In this work, we investigated the electron diffraction pattern of thin C_{60} crystals at liquid helium temperature using a 400 kV cryo-TEM and an imaging plate (IP) to analyze the structure and revealed a disordered structure in the thin crystal. An IP exhibits wide dynamic range, high sensitivity and good linear response to electron dose. These excellent properties make it possible to obtain precise electron diffraction intensities and to analyze crystal structure in atomic resolution.

The thin crystalline sample was prepared by vacuum deposition of C_{60}. The TEM used was JEM-4000SFX, which is equipped with a cryo-stage cooled by liquid helium so that the sample is observed at the temperature of 4.2 K. An electron diffraction pattern with the incident beam along <111> was observed and recorded on an IP. Forty-six integral intensities of symmetrically independent reflections were estimated and compared with those calculated from model structures.

Several workers have carried out the crystal structure analysis on C_{60} below its glass transition point (86K) by X-ray and neutron scattering, where the fitting of the intensity profile was carried out using a rotational angle ϕ as a parameter for the model [4,5], see Fig. 1(a). The best fit was found at ϕ~98°. David [6] analyzed neutron scattering data below the first-order transition point (260K) in detail and pointed out that there are two crystal modifications, which they called the major and the minor orientations, corresponding to different ϕ values. Below the

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Scope of research

Structures of materials and their structural transition associated with chemical reactions are studied through the direct observation of atomic or molecular imaging by high resolution microscopy. It aims to explore new methods for imaging with high resolution and for obtaining more detailed chemical information. The following subjects are studied: direct structure analysis of ultrafine crystallites and ultrathin films, crystal growth and adsorption states of organic materials, and development on high resolution energy filtered imaging as well as electron energy-loss spectroscopy.

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glass transition point the hopping between them is frozen. From their neutron scattering data, the ratio of the major and minor orientations was determined to be ~0.64 at 200 K, which is increased to ~0.84 at the glass transition temperature and becomes constant below that temperature.

At the first step, we discuss the least-squares fit of the observed scattering intensities from the thin C_{60} crystal at liquid helium temperature with those calculated kinematically from a model structure in which all molecules have the same rotation of ϕ. The least-squares fit by the model with a rotation angle was carried out for every degree of the rotation angle. As a result, the R factor reaches the minimum value of 0.23 at ϕ~99°. The rotation angle ϕ~99° coincides well with that of major orientation (97.62°) already reported, which indicates that the C_{60} molecule in thin film tends to have mainly the major orientation at liquid helium temperature.

As the second step of analysis we tried to estimate the coexisting ratio between the major and minor orientations by the least-squares fitting of observed intensities as in the case of David and coworkers. The minimum *R* factor of 0.17 is obtained at major:minor = 0.74:0.26. The ratio of the major orientation, 0.74, is slightly different from the value of 0.84 obtained for the bulk by David and coworkers. The *R* factor is decreased from 0.23 to 0.17 by assuming the coexistence of major and minor orientations.

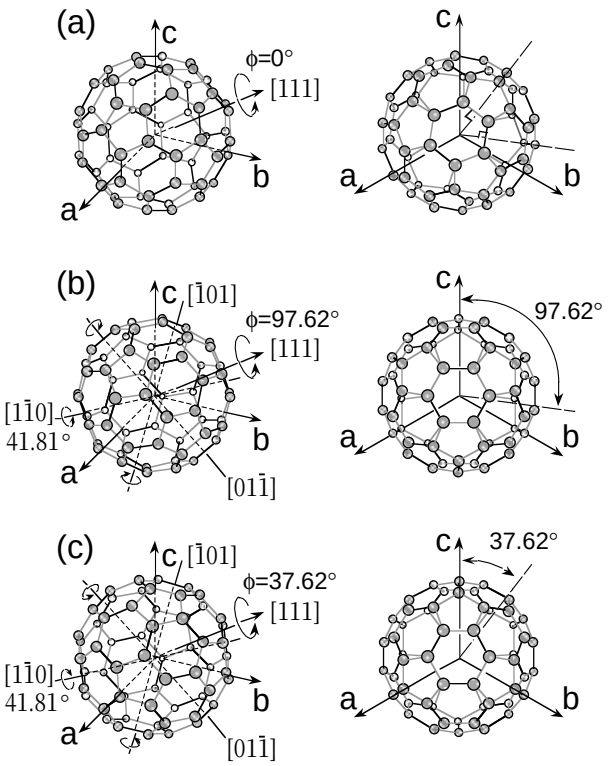

Figure 1. Orientation of the molecule at the origin of the unit cell in the low-temperature phase of C_{60} (left) and their projections on (111) (right). (a) Initial setting, ϕ=0°, where three mirror planes of the molecule is normal to the three unit-cell axes; (b) major orientation, ϕ=97.62°; (c) minor orientation, ϕ=37.62°.

Since the *R* factor of 0.17 still seems unsatisfactory, an extra parameter to be minimized has to be considered. That is, the existence of the f.c.c. component in the sample was considered, where f.c.c. component means an additional disordered region of molecular orientation due to the rapid freezing of molecules at each random orientational angle. The minimum value of *R* factor (0.12) is obtained at the f.c.c.:major:minor ratio of 0.47:0.46:0.07. Accordingly, some molecules are expected to transform into a glassy state without passing through the ordered phase. The major:minor ratio of 0.46:0.07 (= 0.87:0.13) corresponds well to the results of neutron scattering experiment by David and coworkers. The R factor is reduced to 0.12 considering the existence of some fraction of f.c.c.

The specimen used in this work is thin enough and contains no heavy atoms. Therefore the dynamical scattering effect is negligible. However, the *R* factor does not fall lower than 0.23 when an attempt was made to fit the observed intensities only with those calculated based on one structural component structure, *i.e.* major orientation. By assuming the coexistence of minor orientation crystal and also f.c.c. crystal with the random molecular orientation, the *R* factor could be reduced to 0.17 and furthermore to 0.12. The minor orientation and random orientation of f.c.c. structure are regarded as disordered structures in the major orientation crystal. Thus, the structural disorder in a specimen may be one key factor to be considered in structure analysis by electron crystallography.

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